AFRL-AFOSR-JP-TR-2016-0020

Germanate glass fiber lasers for high power

David Lancaster
THE UNIVERSITY OF ADELAIDE

01/04/2016
Final Report

Air Force Research Laboratory
AF Office Of Scientific Research (AFOSR)/ IOA
Arlington, Virginia 22203
Air Force Materiel Command

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
04-01-2016	Final	01-07-2014 to 30-06-2015

4. TITLE AND SUBTITLE
Germanate glass fiber lasers for high power

5a. CONTRACT NUMBER
FA2386-14-1-4033

5b. GRANT NUMBER
Grant 14ION002_144033

5c. PROGRAM ELEMENT NUMBER
61102F

6. AUTHOR(S)
David Lancaster

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
THE UNIVERSITY OF ADELAIDE
115 GRENFELL ST
ADELAIDE, 5000 AU

8. PERFORMING ORGANIZATION REPORT NUMBER
N/A

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AOARD
UNIT 45002
APO AP 96338-5002

10. SPONSOR/MONITOR'S ACRONYM(S)
AFRL/AFOSR/IOA(AOARD)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
14ION002_144043

12. DISTRIBUTION/AVAILABILITY STATEMENT
Distribution Code A: Approved for public release, distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The research reported here details a fundamental investigation of two modified germanate based glasses with a specific focus on glass stability during thermal-cycling which is representative of the steps required to fabricate a doped micro-structured germanate fiber. The investigations revealed for germanate fibres, surface crystallisation is the dominant loss mechanism, and may explain the poor performance of all published germanate fiber lasers. The research team have found a composition of this glass which shows minimal evidence of crystallisation after thermal cycling, and is of a low enough loss to realize a fiber laser. The glass stability is demonstrated by successful fabrication of a small-core rare-earth microstructured fibre fabricated from an extruded germanate preform. The glass bulk loss is measured to be ~ 1 dB/ m at 1.5 m, and ~7 dB/m for the microstructured fiber. Also reported a measurement of the non-linearity of the fibre which indicates its potential suitability for non-linear application such as supercontinuum generation and four-wave mixing.
The research team is confident that germanate based fibers will make substantial impact on the field of heavily doped microstructured fiber lasers operating in the 1.5 to 2.7 m spectral region, if 2low-loss fiber can be realized.

15. SUBJECT TERMS
Germanate fiber Laser, Fiber Laser, Structured Fiber

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Lt Col Kristopher Ahlers
Unclassified	Unclassified	Unclassified	SAR	35	

				19b. TELEPHONE NUMBER *(Include area code)* +81-42-511-2000

AOARD Final Report

Leaky Channel mode germanate glass fiber lasers for high power operation in the short to mid-infrared

Project ID: 144033 RMO File: 2014/4120

Start Date: 15/04/2014 End Date: 30/11/2015

Due Date of Report: 30/11/2015

Prof David Lancaster, Dr Wenqi Zhang,

Laser Physics and Photonics Devices Lab

University of South Australia

and

A/ Prof Heike Ebendorff-Heidepriem, Mr Ahmed Naveed, Ms Jiafang Bei.

Institute for Photonics and Advanced Sensing

University of Adelaide

Report prepared by David Lancaster

Executive Summary

Germanate as a laser host has great potential for realising high-power short infrared lasers from 1.1 to 2.6 um due to wide transparency, low phonon energy, high rare-earth solubility and its suitability for extrusion. However due to material immaturity, and lack of commercial suppliers, these potential advantages have not been realised yet.

The research reported here details a fundamental investigation of two modified germanate based glasses with a specific focus on glass stability during thermal-cycling which is representative of the steps required to fabricate a doped micro-structured germanate fiber. Our investigations revealed for germanate fibres, surface crystallisation is the dominant loss mechanism, and may explain the poor performance of all published germanate fiber lasers. We have found a composition of this glass which shows minimal evidence of crystallisation after thermal cycling, and is of a low enough loss to realise a fiber laser. The glass stability is demonstrated by successful fabrication of a small-core rare-earth microstructured fibre fabricated from an extruded germanate preform. The glass bulk loss is measured to be ~ 1 dB/ m at 1.5 µm, and ~7 dB/m for the microstructured fiber. We also report a measurement of the non-linearity of the fibre which indicates its potential suitability for non-linear application such as supercontinuum generation and four-wave mixing.

We are confident that germanate based fibers will make substantial impact on the field of heavily doped microstructured fiber lasers operating in the 1.5 to 2.7 µm spectral region, if

low-loss fiber can be realised. The glaring reality is that without substantial investment in materials purification to reduce OH^- contamination, and ultimately commercial availability of pure starting chemicals, germanate fiber developed by small university research groups and small companies will struggle to meet application requirements due to high losses causing poor performance.

An attempt was made to achieve laser operation of a holmium doped germanate fiber (GPGN), however due to the high loss of this fiber this has been unsuccessful. We are continuing this project with an aim to better understand the high loss of GPGN fibers.

Contents

1. Introduction

The biggest challenge for researchers working with germanate glass fibre (and indeed all the soft glasses) is the low optical quality of the material which manifests as a high loss and quite fragile fibre. The typical loss of 2 dBm^{-1} illustrates the challenge in creating germanate glass optical fibres with sufficiently pure starting chemicals. The primary reason for the low quality is the use of traditional batching and melting of the constituent materials to fabricate the glass and the commercial availability of insufficiently pure starting materials. The primary absorbing species in the glass have been identified as OH^- and CO_2 radicals with the former radical causing substantial loss between 2.7 μm and the phonon absorption edge at 4.0 μm. In general, precursor purity has limited the efficiency and the emission wavelength from germanate fibre lasers to <2.1 μm.

The aim of this project was to demonstrate a low-loss short-infrared microstructured rare-earth doped fiber laser based on an optimised germanate glass composition.

To fabricate a microstructured germanate fiber laser requires a germanate composition that is stable when subjected to thermal cycling to the glass transition temperature, has low loss, and reduced impurities such as OH^- . There also needs to be a preform extrusion fabrication technique developed to produce the required fiber laser geometry. While our aim was to demonstrate a cladding pumped 'leaky channel mode' (LCM) fiber designed for laser operation, we did end up realising a 'wagon wheel' holmium doped germanate fiber.

At the start of this project we had been working with a lead-germanate glass with a composition labelled as GPLN (GeO_2 – PbO – La_2O_3 – Na_2O). This glass[1] showed promise for both non-linear and laser application. We had previously demonstrated we could produce 'wagon wheel' fiber from this germanate glass composition. However we found that if we tried to produce a more complex microstructured preform from this glass, losses were measured to be ~ 100 dB/m. The detailed post-mortem for this fiber and conclusions are presented and discussed in section 2. This section also discusses the methodology we implemented to investigate the glass stability for an alternate composition of germanate glass we selected.

The focus of section 2 are the results of a thorough investigation of two different germanate glass compositions (particularly network modifiers) to identify a glass composition with high stability (ie. high resistance to surface crystal formation).

The research summary presented here is a comprehensive study of a range of germanate-glasses, where different network formers were added to enhance the stability of the glass. The compositions used were taken from past literature, however we note that this type of comparison study has not been conducted before, to the best of our knowledge.

References

1. H. Tilanka Munasinghe, Anja Winterstein-Beckmann, Christian Schiele, Danilo Manzani, Lothar Wondraczek, Shahraam Afshar V., Tanya M. Monro, and Heike Ebendorff-Heidepriem, "Lead-germanate glasses and fibers: a practical alternative to tellurite for nonlinear fiber applications," Opt. Mater. Express 3, 1488-1503 (2013)

2. Microstructured GPLN germanate fiber loss measurement

To characterise the high loss and poor mechanical property of the microstructrured GPLN, fiber loss measurements were made using a white light source. The result using white light source is shown in Fig.1. In addition, spot loss measurements were applied to double check the fibre loss between 525~1100nm and its results were found in Table 1 and Fig.2. Both results demonstrate the fibre loss was over 100 dB/m ranging from 525~1100nm.

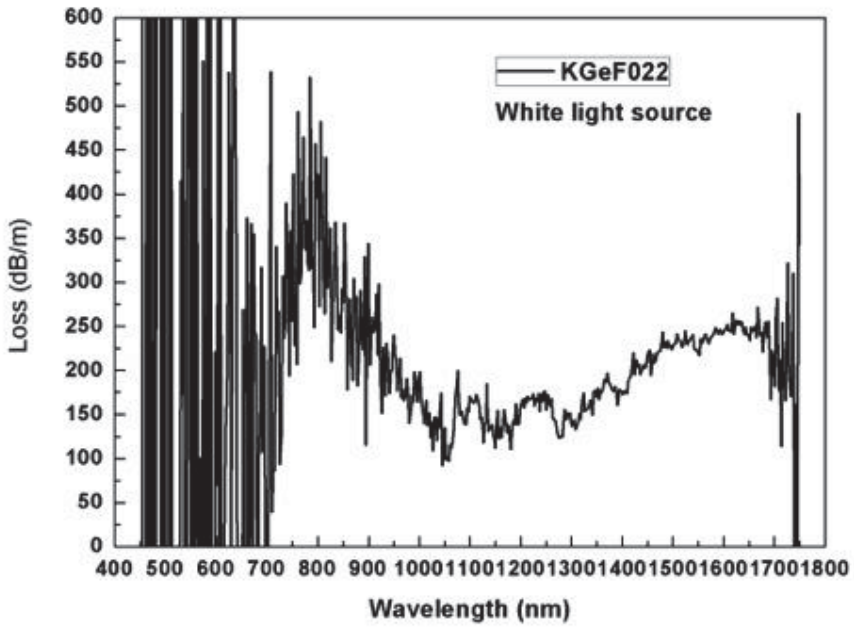


Fig.1. fibre loss of KGeF022 using white light source.

Table 1. results of spot loss measurements for KGeF022.

Wavelength nm	Loss dB/m	R2
525	155.70	0.936
780	154.73	0.930
980	153.00	0.940
1020	155.18	0.940
1050	156.18	0.951
1075	155.41	0.950
1100	155.05	0.949

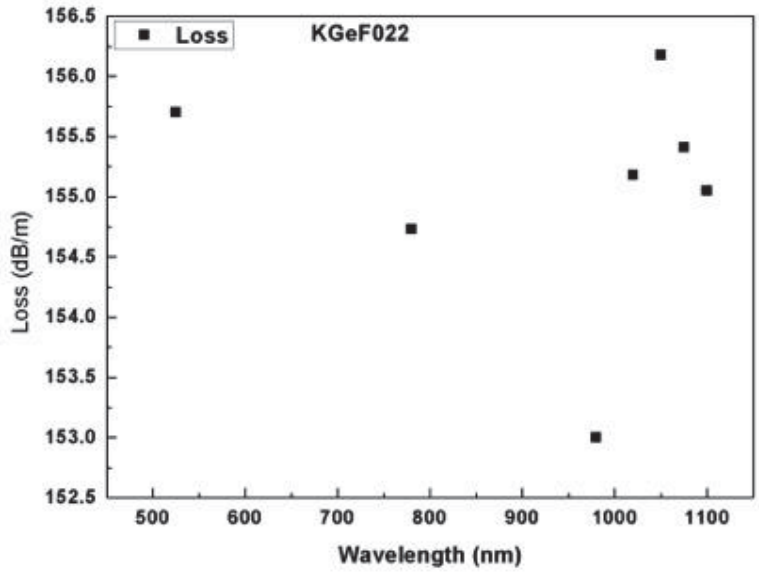


Fig.2. fibre loss of KGeF022 using spot loss measurements.

3. Thermal stability measurement of GPLN glass

- To understand the reasons for this high loss in these fibers, we undertook a study of various germanate based glasses under temperature cycling.
- Hypothesis: Thermal cycling produces nano-crystal formation.

Differential scanning calorimetry

DSC measures the glass transition (Tg) and the glass crystalisation temperature (Tx) – the greater the difference the more stable the glass is.

The following compositions were used, with melting conditions also listed :

- KGe024: $60GeO_2$-xPbO-$y$$La_2O_3$-$z$$Na_2O$ doped with 0.09mol% HoF_3 (glovebox)
- KGe026: $60GeO_2$-aPbO-$b$$La_2O_3$-$c$$Na_2O$ (open air firstly then glovebox melting for dehydration)
- KGe027: $60GeO_2$-aPbO-$b$$La_2O_3$-$c$$Na_2O$ (open air)

Table 1. Results of DSC

	Tg (^oC)	Tx(^oC)
KGe024	463	650
Kge026	417	672
Kge027	417	662

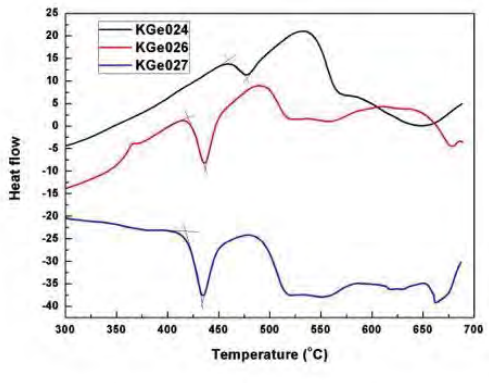


Fig.3. DSC of Kge024,026 and 027.

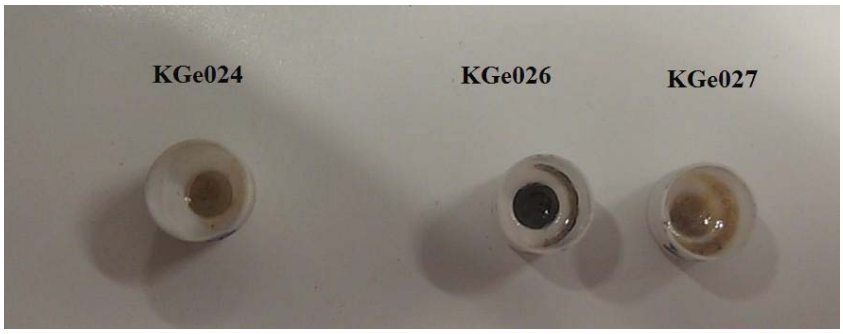
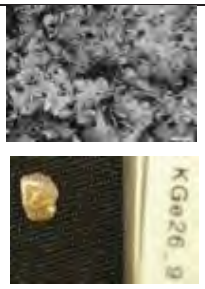


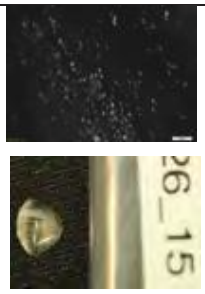
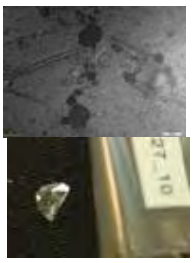
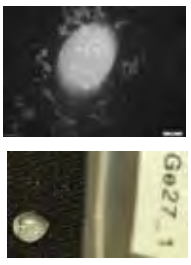
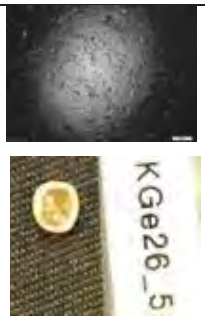
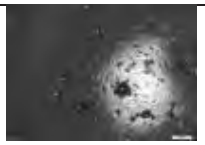
Fig.4. image of residual glass of Kge024,026 and 027 after DSC.

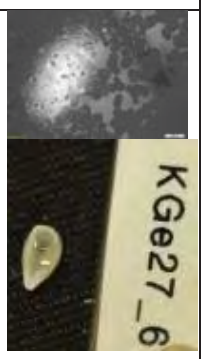
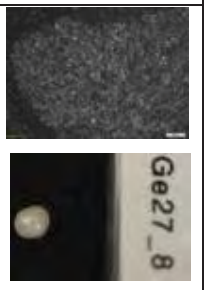
The black glass in KGe026 after DSC (Fig.4) indicates the reduction of Pb.

Annealing test

All slides became opaque after annealed either in glovebox or open air furnace.

condition		KGe026 Slide No	KGe027 Slide No	After annealing	
				KGe026	KGe027
Glovebox-562 °C	10min	10	2		
	30min	9	3		
	50min	8[a)]	4[a)]		

Open air 562 °C	10min	15	12		
	30min	14	11		
	50min	13	10		
Glovebox 522 °C	2.5 hour	1	1		
Glovebox 520°C	8 hour	5	5		
Glovebox 515°C	6 hour	7	7		

					
Glovebox 519°C	4hour	6	6		
Open air 520°C	8 hour	12	9		
Open air 515°C	6 hour	11[b)]	8[b)]		

a) samples were used for SEM.

b) samples were used for XRD after annealing.

SEM tests

KGeF21 and 22

Higher surface roughness was found on the outer surfaces of fibres compared to internal surfaces(Fig.5 &7).

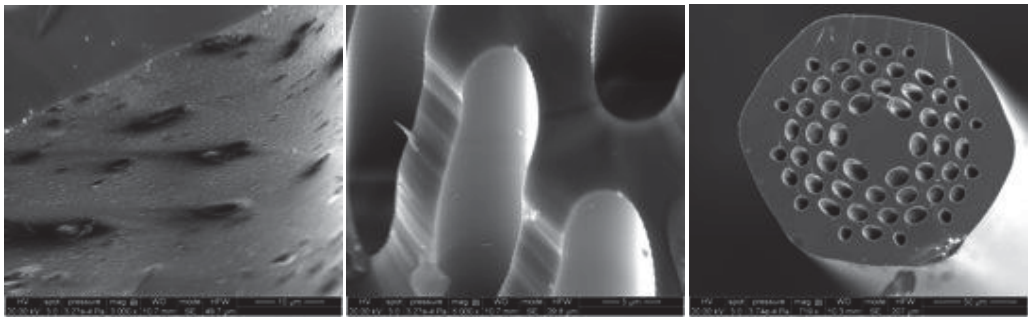


Fig.5. SEM image of KGeF021

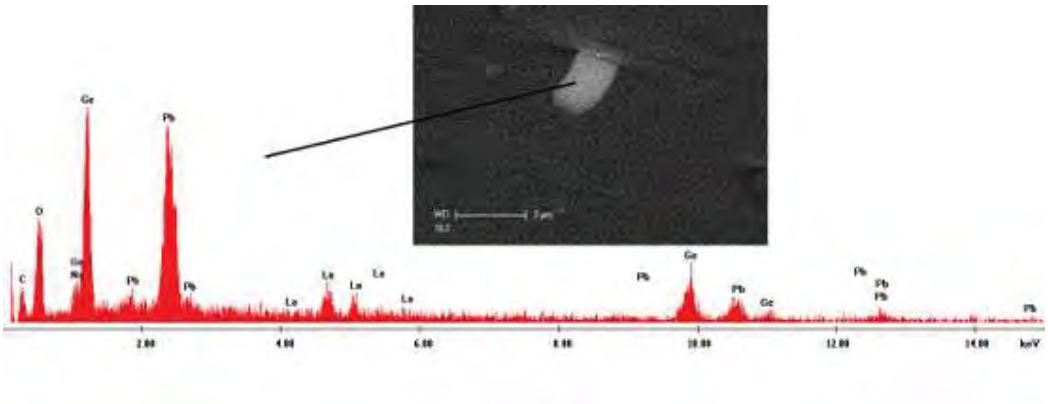


Fig.6. EDX image of KGe0F21 (surface scatter).

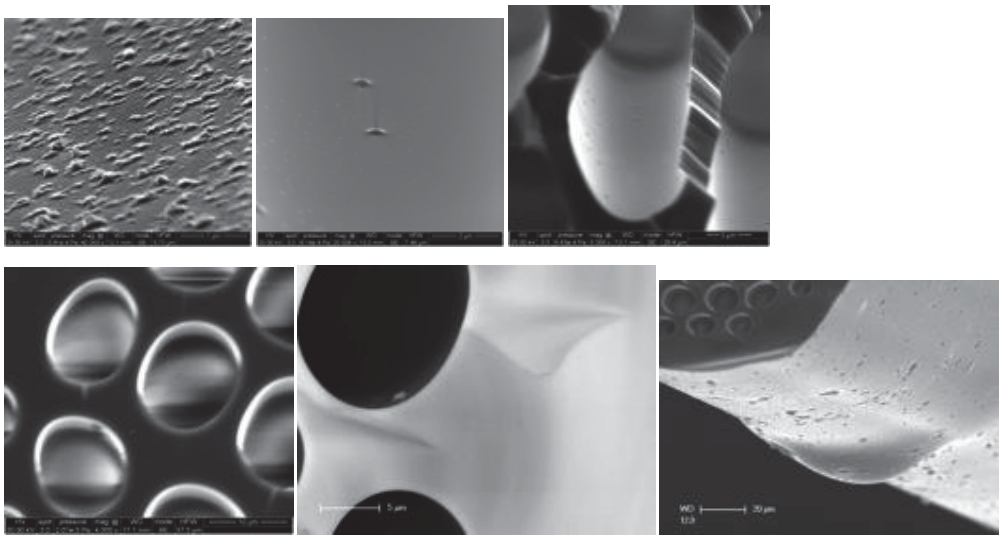


Fig. 7. SEM image of KGeF022.

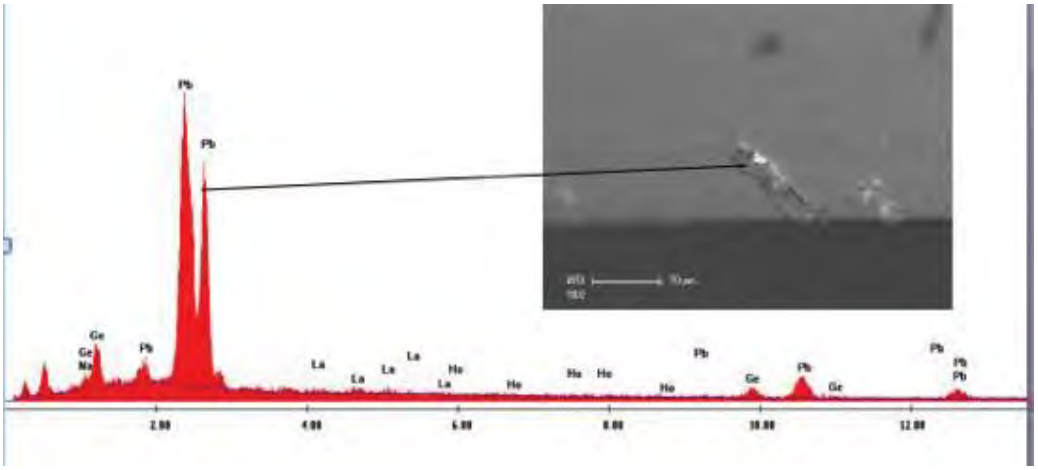


Fig.8. EDX image of KGeF022 (surface scatter).

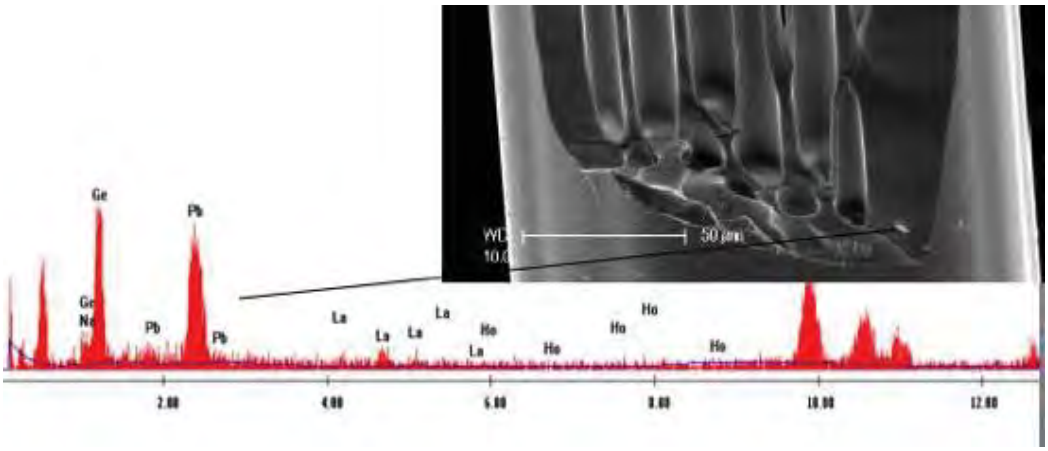


Fig. 9. EDX image of KGeF022 (white particle in the hole).

KGe026 and 027 after annealing at 562 °C for 50 mins

High content of Pb was found in the defects after annealing.

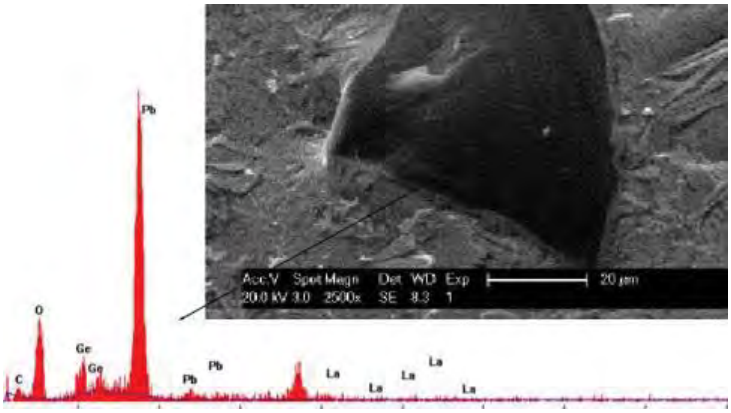


Fig. 10. EDX image of KGe026 (black part).

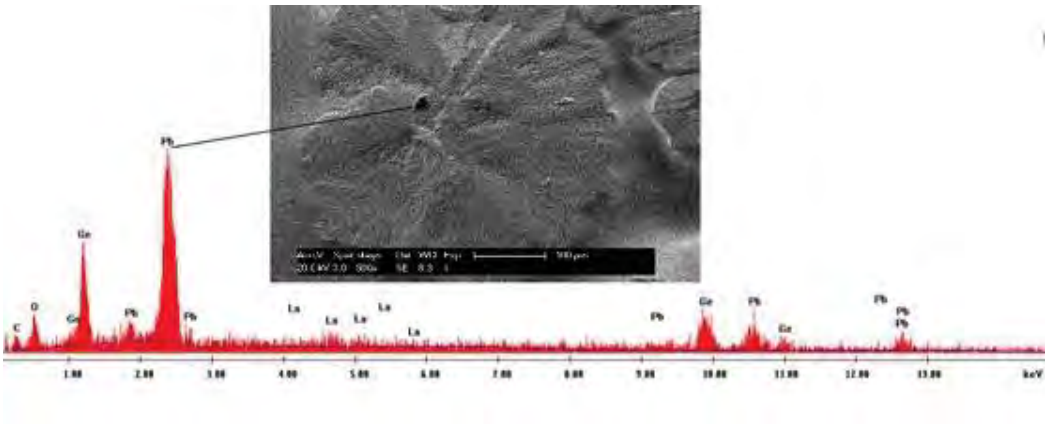


Fig. 11. EDX image of KGe026 (black part).

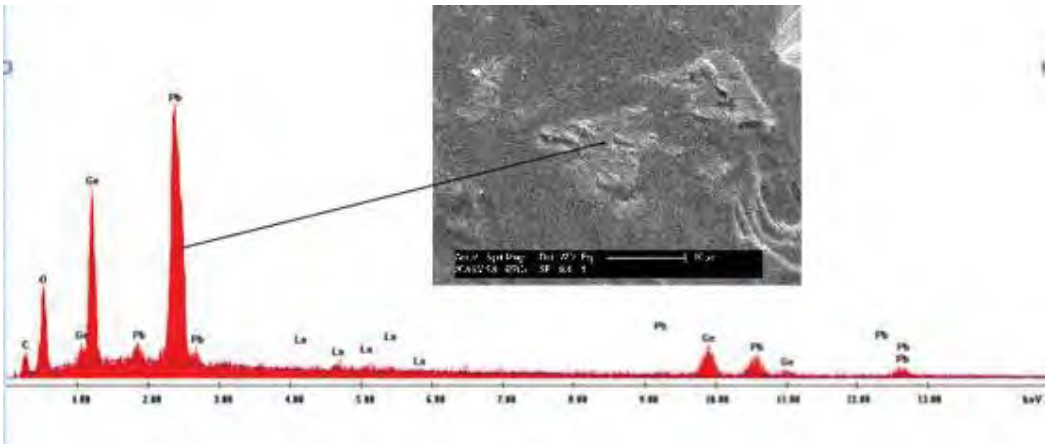


Fig. 12. EDX image of KGe027 (grey part).

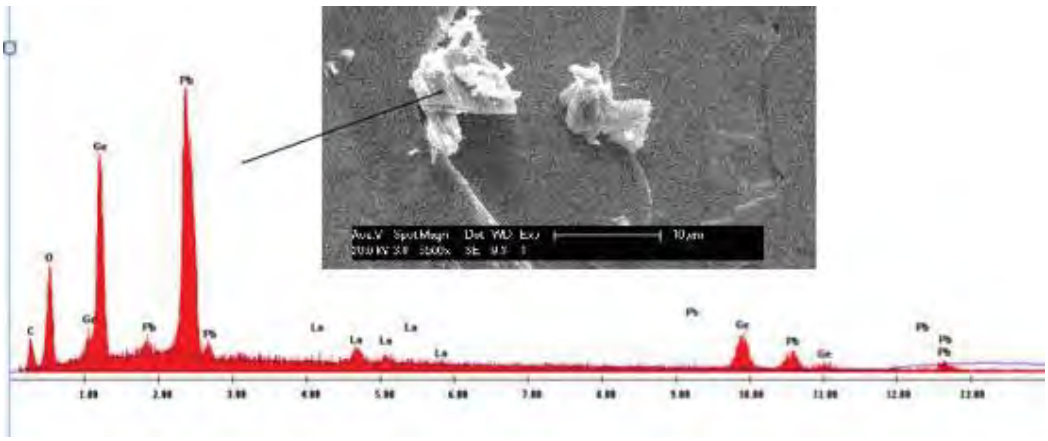


Fig. 13. EDX image of KGe027 (white part).

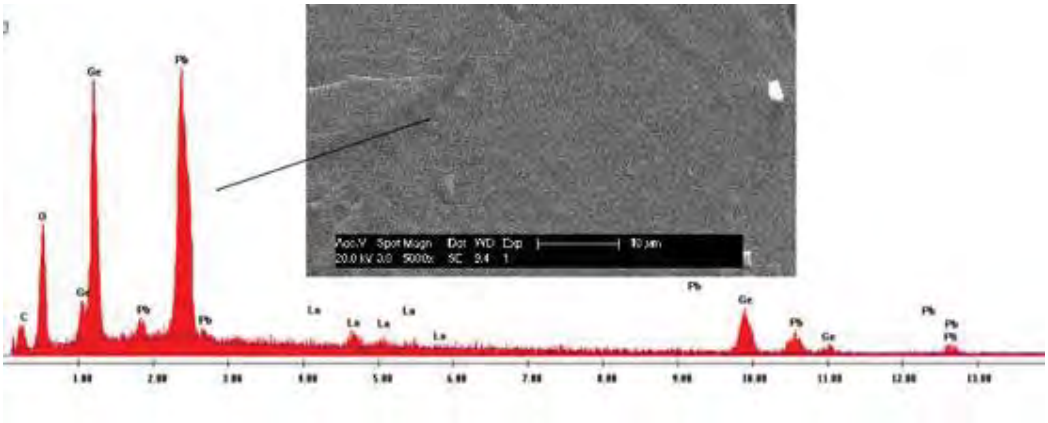
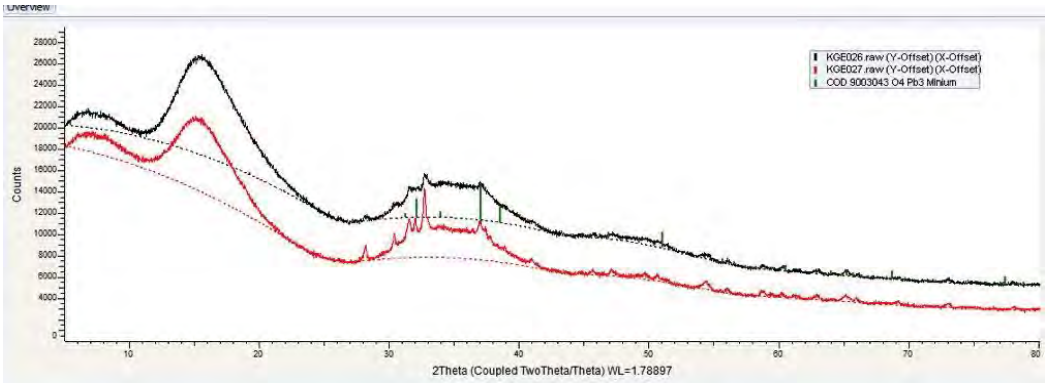


Fig. 14. EDX image of KGe027 (glass part).

XRD

- Both KGe026 and 27 after annealed contained crystalline Pb_3O_4. It indicates the reduction of Pb in glass after annealing.



Summary 1: The data supports our hypothesis that the high loss of these glasses after additional thermal processing (such as due to extrusion and drawing into fibers) is due to formation of nanocrystals of Pb_3O_4.

4. Investigation of modified germanate glasses to reduce/ eliminate nanocrystal formation.

As the reduction of lead was found in the previous germanate glass (KGe027) at extrusion and fibre drawing conditions, two new compositions (KGe028 &029) were chosen for glass melting in the lab.

KGe027: 60GeO_2-*a* PbO-*b* La_2O_3-*c* Na_2O (GPLN[1])

KGe028: 56GeO_2-*d* PbO-*e* Ga_2O_3-*f* Na_2O (GPGN[2])

KGe029: 55GeO_2-*g* PbO-*h* BaO-*I* ZnO-*j* K_2O (GPBZ[3])

Table 1. Details of three glasses

	Density (g/cm^{-1})	Glass weight (g)	Evaporative loss	T_g (°C) (from reference)	T_g (°C) (from reference)
KGe027	5.83	18.570	1.35%	415[1]	663[1]
KGe028	5.62	16.288	1.60%	387[2]	---
KGe029	5.23	11.377	1.23%	465[3]	665[3]

--- all the glasses were melted at open air condition at 1250 °C for 75min.

--- CO_2 mass loss was deducted from the evaporative loss.

1. H. T. Munasinghe, A. Winterstein-Beckmann, C. Schiele, D. Manzani, L. Wondraczek, S. Afshar V, T. M. Monro, and H. Ebendorff-Heidepriem, "Lead-germanate glasses and fibers: a practical alternative to tellurite for nonlinearfiber applications," Optic. Materials Express **3**, 1488-1503 (2013).

2. X. Jiang, J. Lousteau, B. Richards, and A. Jha, "Investigation on germanium oxide-based glasses for infrared optical fibre development," Optical Materials **31**, 1701-1706 (2009).

3. J. Wang, J. R. Lincoln, W. S. Brocklesby, R. S. Deol, C. J. Mackechnie, A. Pearson, A. C. Tropper, D. C. Hanna, and D. N. Payne, "Fabrication and optical properties of lead - germanate glasses and a new class of optical fibers doped with Tm^{3+}," Journal of Applied Physics **73**, 8066-8075 (1993).

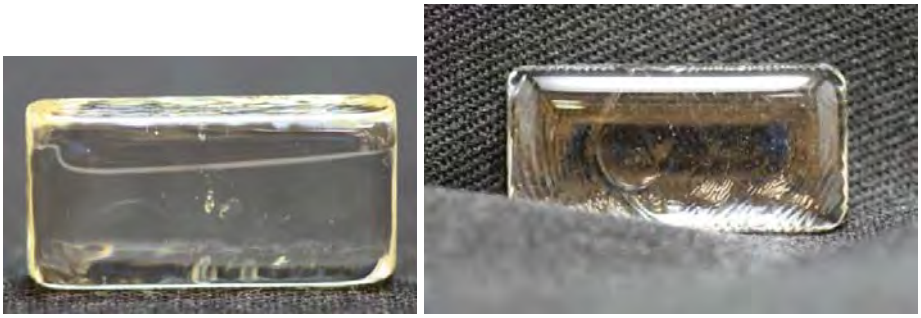


Fig.1. image of KGe028 - GPGN (left) and KGe029 - GPBZ (right)

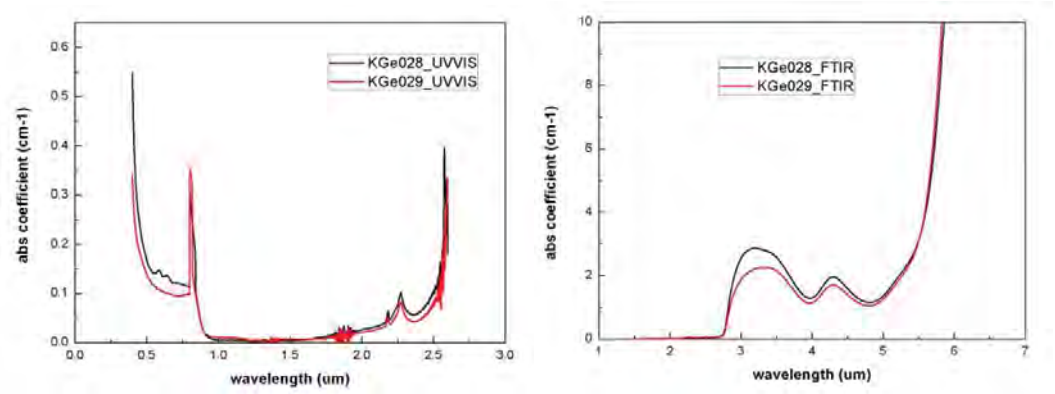


Fig.2. absorption coefficients of KGe028 (GPGN) and KGe029 (GPBZ)

Annealing tests of KGe024 to KGe029

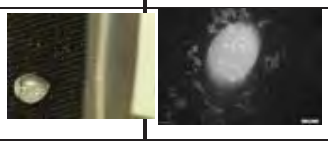
1. Differential Scanning Calorimeter measurements

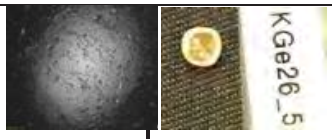
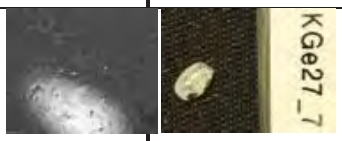
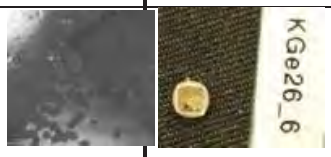
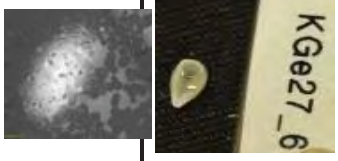
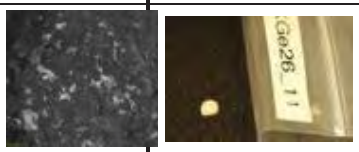
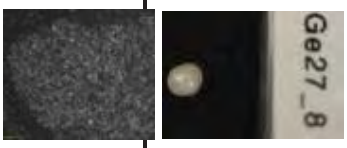
	Tg (°C)	Tx(°C)	Appearance of crucible after DSC
KGe024	463	650	Brown, small black dots
KGe026	417	672	black
KGe027	417	662	Brown, small black dots
KGe028	387[1]	---	
KGe029 &30	465[2]	665[2]	

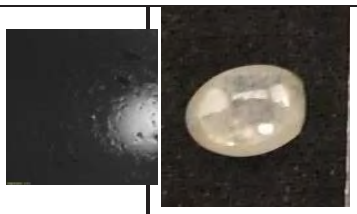
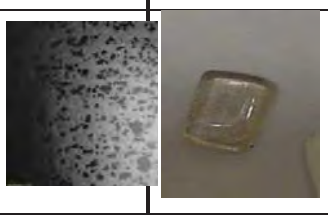
Table 1. Results of DSC

- To determine crystallisation susceptibility, qualitative estimations were made of the degree of crystallisation that occurred after high temperature annealing for ~ 6 hours.

2. Annealing Tests

No	condition		deformation	crystal	After annealing
KGe026_1	Glovebox 522 °C	2.5 hour	yes	++++	
KGe027_1			yes	++++	

KGe026_5	Glovebox 520°C	8 hour	yes	+++++	
KGe027_5			yes	+++++	
KGe026_7	Glovebox 515°C	6 hour	yes	+++++	
KGe027_7			yes	+++++	
KGe026_6	Glovebox 519°C	4hour	yes	+++++	
KGe027_6			yes	+++++	
KGe026_12	Open air 520°C	8 hour	yes	+++++	
KGe027_9			yes	+++++	
KGe026_11	Open air 515°C	6 hour	yes	+++++	
KGe027_8			yes	+++++	

KGe028_1	Glovebox 484.4°C	6h	Yes	+++	
KGe028_2	Glovebox 468.8°C	6h	Yes	++	
KGe029_1	Glovebox 539°C	6h	No	+++++ two kinds of crystals	
KGe030_1			No	+++++	

Conclusions:

- Composition KGe028 (GPGN) was found to exhibit substantially less crystal formation than all other Ge glass compositions studied.
- Next stage glass fabrication: To reduce loss, compositions of glass based on GPGN (kGe028) were fabricated in the dry glove box to further reduce OH- contamination.

Fig. 3. Billets of GPGN glass

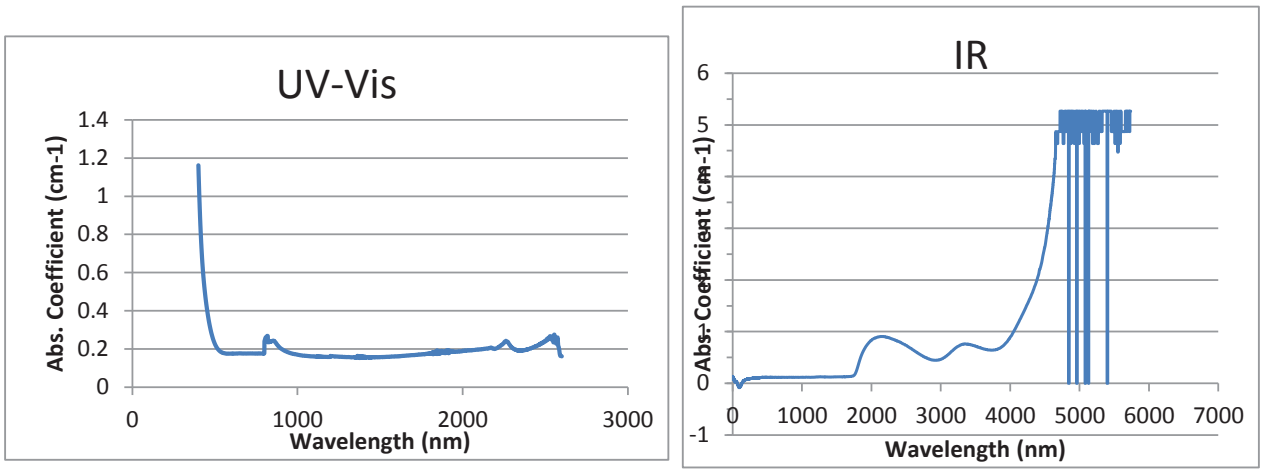


Fig. 4. Measured loss of GPGN glass

References:

1. Spectroscopic properties of bismuth-germanate glasses co-doped with erbium and holmium ions, Tomasz Ragin, Marcin Kochanowicz, Jacek Zmojda*, Dominik Dorosz
2. Fluorogermanate glass with reduced content of OH-groups for infrared fiber optics, Xin Jiang, Joris Lousteau, Shaoxiong Shen, Animesh Jha, doi:10.1016/j.jnoncrysol.2009.04.069)

5. Fabrication of a modified GPGN germanate glass

Melt quench fabrication of low-loss germanate based glass for laser and non-linear application

This chapter covers the fabrication of the glass we have identified to have the highest glass stability: GPGN glass.

Introduction

A number of different laser technologies can be used to access the mid-infrared spectral region. Typically considered to cover the wavelength range of 3–10 µm, this region is particularly important for applications such as gas sensing and spectroscopy, with many molecules and chemical compounds having strong absorption lines. [1]

Among oxide glasses used for mid IR applications, it is observed that Germanate glasses have similar phonon energies and mid-IR transmission properties when compared to tellurite glasses, but they are better than tellurite glasses in terms of thermal and mechanical stability based on previous demonstrations. *[2,3]* In the lead-germanate glass experiments, brief research was done on a GPLN ($60GeO_2$-$33PbO$-$2La_2O_3$-$5Na_2O$) composition. Low thermal stability and greater tendency towards crystal formation during fiber drawing, has shifted the attention to GPGN (56GeO2-31PbO-4Ga2O3-9Na2O) composition, which showed promising results for the fiber drawing. The most crucial concern in fabricating such a fiber is getting a bulk glass with low OH loss, as the presence of OH in the glass causes absorption at the 3um range. Experiments have been carried out in the past in an attempt to reduce the OH loss in germanate glass by introducing longer melt times, raw material drying and addition of PbF2 in the glass composition. [4*]* While the first two steps have proven to help reduce OH loss without affecting glass properties, addition or replacing raw materials with PbF2 has been demonstrated to reduce the thermal stability of the glass. [5] The aim of this work is to reduce the OH loss of the glass to enable fabrication of a microstructured fibre for laser application. Focus has been towards the MOF for ease of fabrication and to avoid the need for different glass compositions for the core and cladding. A microstructured fibre has more design flexiblity than a standard index guide core-clad fibre. As a proof of concent we are working towards demonstrating a short-infrared holmium doped fibre that may be superior to silica due to easier fabrication and the lower phonon energy of germanate compared to silica. This geometry also has potential for supercontinuum generation due to the high non-linearity of germanate glass.

This will need to cover the work done to date in germanate glass for fibre development as well as efforts at purification. What other approaches have people used to reduce losses ? What are the biggest challenges in this area ? You will certainly need a good reference list here (as a first step it will be worth identifying the papers that need to be referenced. The aim of this work is to reduce the loss of the glass to enable fabrication of a low-loss microstructured fibre for laser application. We also need to introduce why we have investigated this composition compared to GPLN, as well as reference the prior work on GPGN.

Experimental

Melting details and composition

Lead-Germanate glass with composition 56GeO2-31PbO-4Ga2O3-9Na2O was used for thermal and optical characterization. 30g batches of sample were mixed in an ultra-dry glovebox atmosphere with less than 0.1ppm of water. Raw materials in the form of powder with high purity (GeO2 – 99.999%, PbO – 99.99%, Ga2O3 – 99.995 and Na2CO3 – 99.997%) were used. Batched samples were then transferred to a Platinum crucible and melted at 1250oC for 1-2.5 hours in a dry Oxygen, dry

Nitrogen/ Oxygen, dry Nitrogen or ambient atmosphere. Raw material drying at 500oC in N2 atmosphere was introduced in some of the batches in order to study the loss due to OH absorption. To get a homogenous mixture, the crucible was swirled between the melt, resulting in a bubble-free glass. The melts were then poured into a 15x30mm mold and annealed in dry N2 or ambient atmosphere for 2 hours at temperature close to the glass transition temperature. Annealed blocks or billets were then polished for optical characterization.

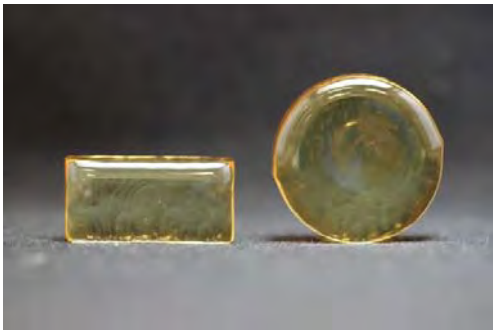


Fig. 1. Photograph of GPGN glass as 15x30mm block and 30mm diameter billet after annealing

Sample Characterization

Around 50mg from prepared glass was crushed into fine powder and placed in an alumina crucible for thermal analysis using a Perkin Elmer STA8000 in the range of 300-800oC in an ambient atmosphere with a heating rate of 10oC/min. Based on the exothermic and endothermic peaks resulting from the plot, Tg and Tx were calculated. The calculation of Tg and Tx helped in determining the preform extrusion and fiber drawing temperature limits and also the thermal stability of the glass ($\Delta T = Tx - Tg$).

UV-Vis and FTIR spectroscopy were done on the polished surface of glass sample with thickness 3-4mm using a CARY 5000 UV-Vis spectrophotometer and Perkin Elmer Spectrum 400 FTIR spectrometer respectively. The spectrometers covered the measuring wavelength range from 0.4 – 10um. The resulting plots were used to calculate the OH- absorption at 3um after subtracting losses due to Fresnel reflections.

Annealing tests on 5x5mm of prepared glass were done at varying controlled temperatures and atmospheres, to check if glass would crystallize during extrusion or fiber drawing. Samples were placed in open air/ dry N2/ dry O2 atmospheres in the temperature range of 450oC to 515oC for a period of 6 hours, to mimic extrusion conditions. Annealed samples were checked under the microscope to detect formation of crystals. X-ray diffraction (XRD) measurements were run on the crystallized samples to detect the composition of the crystals formed at different conditions.

Fiber fabrication and characterization

For the purpose of fiber drawing batches of 100g doped with 0.8mol% of Ho2O3 were melted at 1250oC in dry O2 atmosphere for 5h and annealed at glass transition temperature in N2 atmosphere for 2 hours resulting in billets of 30mm diameter. Prepared glass billets were extruded into 10mm diameter rods at around 455oC with an extrusion rate of 0.2mm/min in N2 atmosphere. Rods of good quality were obtained for fiber drawing. Microstructured core preforms and outer tubes were extruded and caned to allow the desired fibre geometries to be produced.

Fiber was typically drawn at 515oC by placing the preform at the top of the furnace and dropping it to the heating zone, resulting in a glass drop followed by the fiber, which was wound on a motorized drum. The fiber diameter was maintained at 160um by controlling the drum speed and temperature of the furnace. More than 50m of fiber could be obtained from a 100g glass melt. Based on fiber drawing tests performed on the GPGN glass, the most suitable atmosphere was found to be 90:10 N2:O2. The presence of small amount of Oxygen helps in preventing the reduction of Lead, which is evident by the presence of black particles in the drawn glass.

Losses in the fiber were measured using the cut-back method between the wavelength range of 350-1750nm using a bulb and UV-Vis spectrum analyzer. Total cutback of up to 5m was done in a series of smaller cutbacks of 1 to 1.5m and the detected signal from the emitting end of the fiber was used to calculate fiber loss in dB/m. In order to maintain consistency at each cutback, three 0.07m cutbacks were done for every 1.5m cutback of the fiber, to ensure that varying cleaving angles did not impact the transmission efficiency.

Results and discussions

Sample Code	Melting atmosphere	Raw material drying (h)	Melt duration (h)	Mass loss after melt (g)	Density (g/cm ^3)	Tg (oC) (why so many blanks?)	Tx (oC)	Loss at 3um (dB/m)
KGe028	Open air	-	1:10		5.61	376	533	1222
KGe049	O2	-	1:10		-	387	-	179
KGe034	N2/O2	-	1:10		-			184
KGe035ᴴ	O2	-	1:10		5.497	-	-	263
KGe037ᴴ	O2	1	1:10		5.483	-	-	107
KGe047ᴴ	O2	17	1:10		5.500	-	-	94
KGe046ᴴ	O2	-	2:30		5.478	-	-	99
KGe052ᴴ	N2	-	1:10					87

ᴴ = doped with 0.08mol% Ho2O3

Thermal properties of glass

DSC curves of GPGN composition melted in O2 and open air are shown in figure. The resulting DSC curves showed a Tg of 390oC and no prominent Tx peak for the glass melted in dry O2 atmosphere. This suggested that the glass composition GPGN was very stable against crystallization during the extrusion or fiber drawing steps. The addition of Gallium in the glass compositions seemed to enhance the stability of the glass, providing a wider window for experimenting with glass extrusion and fiber drawing temperatures. The glass melted in ambient atmosphere (KGe028 ?) showed lower thermal stability, ΔT=157oC. The GPGN glass composition obtained in the alumina crucible after the DSC runs was clear with no residue or crystal formation.

(This part to include the DSC curves of 4 samples melted in N2, O2, N2/O2 and open air. I will also include some images of crystal formation in different glasses at similar temperatures)

Loss due to OH at 3um

The transmission data from UV-VIS and FTIR spectroscopy was used to calculate loss in dB/m at ~3um due to the OH-. Losses due to Fresnel reflection in samples due to anomalies in the polishing have been subtracted in all the spectra. Based on the loss calculated, the following steps helped in reducing the OH-absorption at 3um.

Melting atmosphere

The melting atmosphere has an impact on the OH peak, glass transition temperature as well as the crystallization tendency of the glass during extrusion and fiber drawing steps. The batch melted in ambient atmosphere showed loss at ~3um as high as 1222dB/m and a lower thermal stability with T_g of 376^{o}C and T_x of 533^{o}C. The open air melt also caused the glass to crystallize during the re-heating at temperatures starting from 459^{o}C, which is the extrusion temperature for the glass. Based on the observations, melting of GPGN glass in ambient atmosphere was not a suitable option. Another 30g batch was melted in dry N_2/O_2 atmosphere with gas ratios of 80:20, which resulted in lower OH absorption at ~3um, but showed rod-shaped crystal formation at the extrusion temperature. In order to avoid the scattering loss due to crystal formation in the fiber, melting in N_2/O_2 atmosphere was not experimented with any further. Another batch was melted for the same duration in dry N_2 atmosphere. This glass showed the lowest OH loss, but formed black particles on reheating at the extrusion temperature. In order to avoid crystals during fiber fabrication, a different melting atmosphere was chosen. Glass melted in dry O_2 atmosphere showed lower loss at ~3um when compared to open air melts, but similar to melts done in a mixture of N_2/O_2 atmosphere. The resultant glass showed the least crystallization at 480^{o}C, which meant that crystal-free preforms could be extruded for fiber fabrication. One obvious reason for the difference between the open air and ultradry glovebox melts is the amount of water contained in the melting atmosphere. Melts in controlled glovebox atmospheres with less than 0.1ppm of water, leave lesser moisture to react with the glass composition during melt. (The resistance to crystallization in glasses melted in 100% O_2 atmosphere could be attributed to the presence of abundant bridging oxygen atom present in the glass structure, effectively delaying the devitrification process). Details of the four batches melted in different atmospheres is presented in Table 1 and the resultant OH loss in Fig. 3.

Table 1. Details of glass batches melted in different atmospheres. All samples melted at 1250oC for 70 mins.

Parameters	KGe028	KGe049	KGe034	KGe052

Composition	GPGN	GPGN	GPGN	GPGN[H]
Melting atmosphere and gas flow	Open air	4L/min O2	3.2L/min N2, 0.8L/min O2	4L/min N2
Crystal formation at extrusion temperature	Yes	Partial	Partial	Back particles throughout the surface
Loss at 3um	1222 dB/m	179 dB/m	184 dB/m	87dB/m

[H] = doped with 0.08mol% Ho2O3

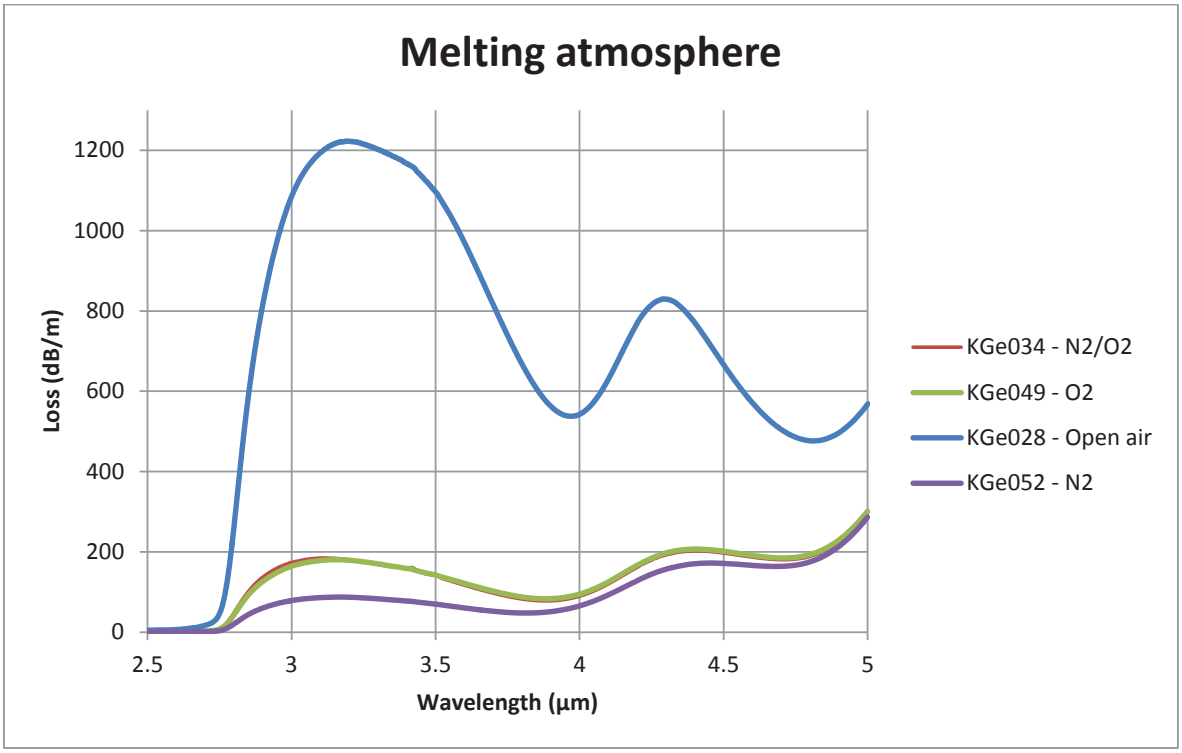


Fig. 3. Loss due to OH absorption for samples melted in different atmospheres

Raw material dehydration

Drying of raw materials (Table 2) at 500°C in N_2 atmosphere for 1 hour in an open platinum crucible showed lower loss as the moisture from the raw materials was removed before it could react with the glass composition during the melting step. After one hour of drying, the gas flow was changed from N_2 to O_2 and a platinum lid was used to cover the crucible for the melting process. To compare the change in OH loss with and without the drying step, raw material drying was done just for one hour. Longer drying durations did not show much reduction in OH absorption, as all the moisture which could possibly be removed from the

raw materials at 500oC, is removed within the first hour of the drying process. Maximum dehydration temperature of 500oC was chosen so as to not affect the chemical properties of the raw materials before the melt. Comparison of samples with the raw material dehydration step is presented in Table 2 and absorption spectrum in Fig. 4.

Table 2. Details of glass batches melted with different raw material drying durations. All samples melted at 1250oC for 70 mins in a 100% O2 atmpsphere.

Parameters	KGe035	KGe037	KGe047
Composition	GPGN – Ho+	GPGN – Ho+	GPGN – Ho+
Raw material drying	No	1hr at 500oC in N2 atmosphere	17h at 500oC in N2 atmosphere
Loss at 3um	263 dB/m	107 dB/m	94 dB/m

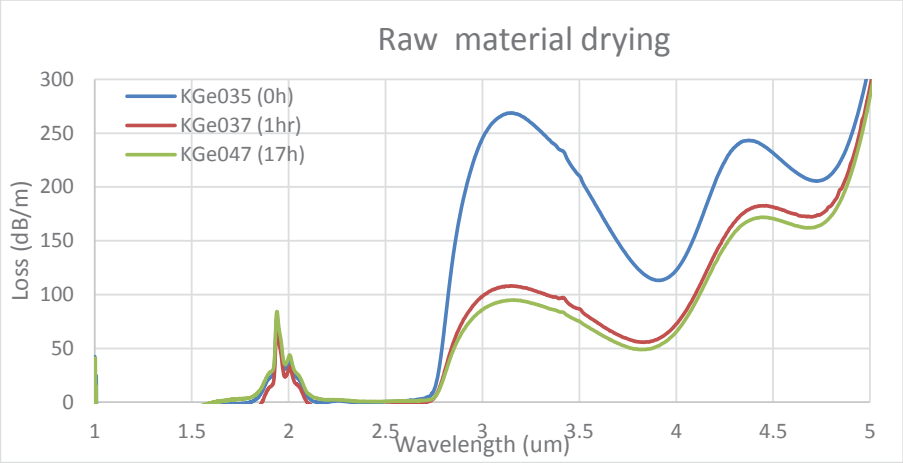


Fig. 4. Comparison of samples with different raw material drying steps

Melting duration

Increasing the melting duration showed lower OH absorption. This is because the glass melt goes through a water removal reaction which requires a minimum amount of time to complete [5]. Apart from temperature, this reaction is also related to the duration for which the melt has been placed in the furnace. As the duration increases, the OH absorption in the spectrum reduced further. Given in Table 3 and Fig. 5 are the melt details and loss spectrum respectively.

Parameters	KGe035	KGe046
Composition	GPGN – Ho+	GPGN – Ho+

Melting duration	70 mins	150 mins
Loss at 3um	263 dB/m	99 dB/m

Table 3 Details of glass batches melted for different durations. Both samples were melted at 1250oC in a 100% O2 atmosphere.

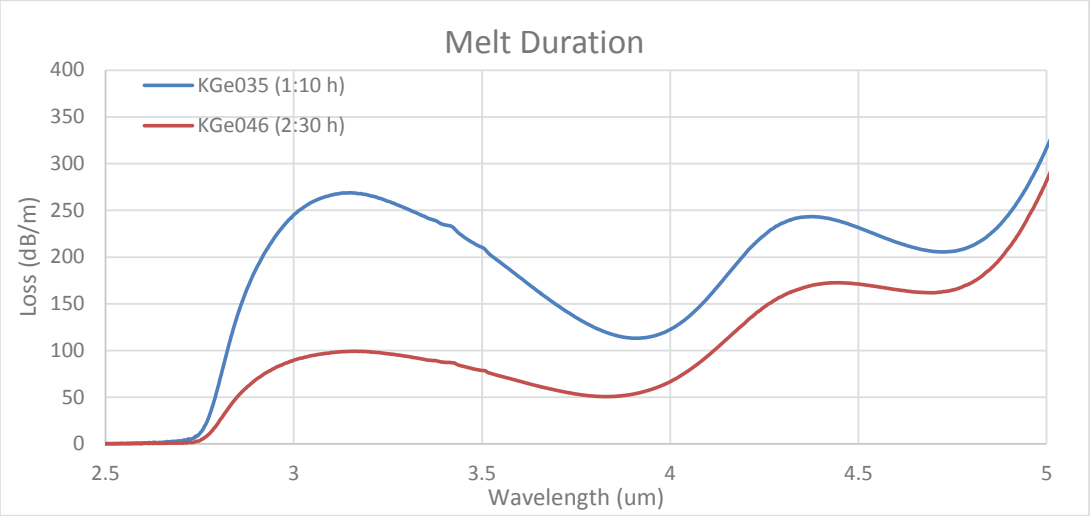


Fig. 5. Comparison of samples with different melting durations

1.2.1 Glass remelt and interaction with melting atmosphere

Drastic effect on the OH absorption was also noticed when the glass was re-melted. This could result from the complete removal of OH containing atmosphere within the melting furnace and the fresh flow of dry gas, which removes more OH- from the glass composition. Based on the observations from the re-melt, experiments are to be done with increased interaction between the atmosphere inside and outside the crucible. Fig. 6 shows the comparison of sample KGe051 melted in 100% N2 for 70 mins and then remelted in the same atmosphere for the same duration after cooling down.

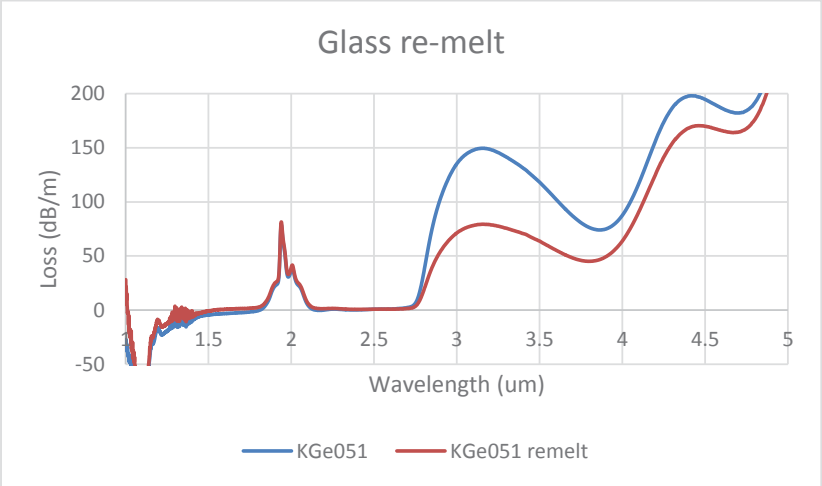


Fig. 6. Effect of re-melting glass for 1.5h after it has cooled down.

Interaction between the glass melt and the melting atmosphere has an impact on the amount of OH contained in the cast glass. Two separate samples were melted with crucible lid completely closed and with the lid half open. Table 4 and Fig. 7 give details of the melt and the resulting loss curve respectively.

Table 4 Melt parameters of glasses melted with different lid positions. Both samples were melted at 1250oC for 70 mins in a 100% O2 atmosphere.

Parameters	KGe049	KGe053
Composition	GPGN – Ho+	GPGN – Ho+
Lid position	Fully closed	Half open
Loss at 3um	178 dB/m	134 dB/m

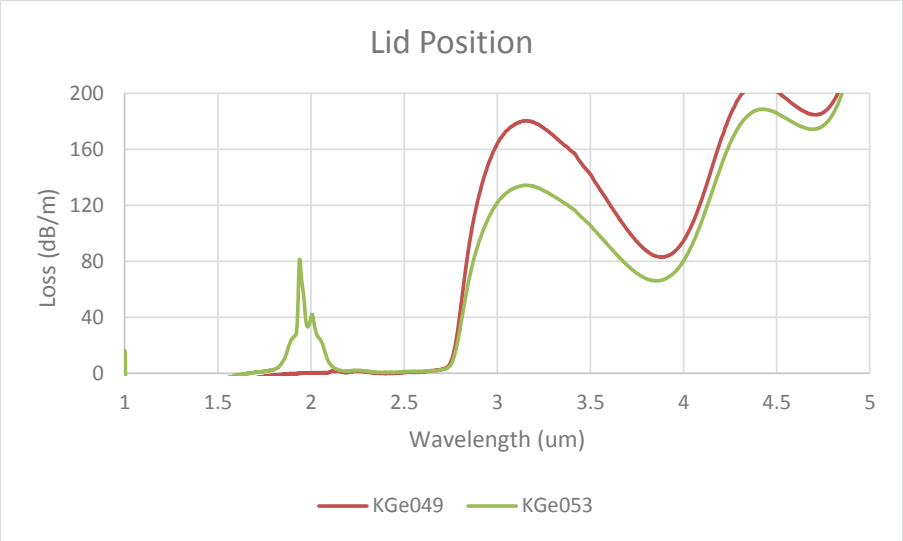


Fig. 7. Loss curve depicting the effect of interaction between raw material and melting atmosphere during the melt

1.2.2 Replacing 5mol% of PbO with PbCl2

Substitution of 5mol% of PbO with PbCl2 showed a drastic reduction in OH absorption using the same melting conditions. This can be explained by the reaction:

Cl- + OH- = HCl + O2-

It is important to note that there is a certain amount of time required for the reaction to complete. If the composition continues to stay in the furnace after the reaction has taken place, the OH- forms again in the glass composition as no Cl- ions remain to react with it and escape as HCl. On the other hand, if the melt is ended before the reaction has completed, most of the OH- fails to react with Cl- ions and remain in the glass contributing to higher absorption at 3um. It is therefore essential to find

the right amount of time required to effectively remove the OH- from the glass. Given in Fig. 8 are the loss curves of different samples containing 5mol% PbCl2 melted for different durations. All the samples were melted at 1250oC in a 100% O2 atmosphere. As noticed from the Fig. 9 the samples follow a trend that can justify the above hypothesis.

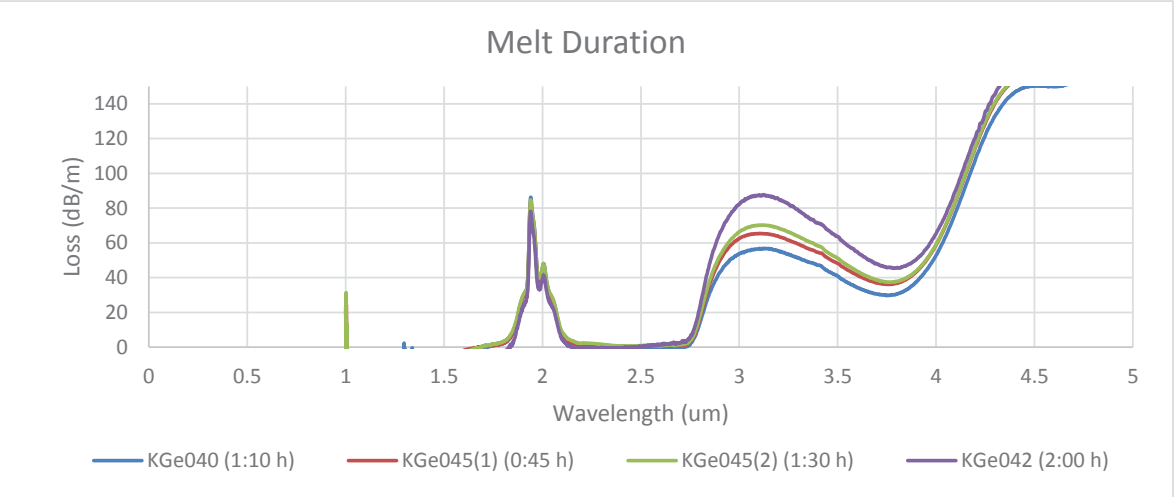


Fig. 8. Samples containing 5mol% PbCl2 melted for different duration.

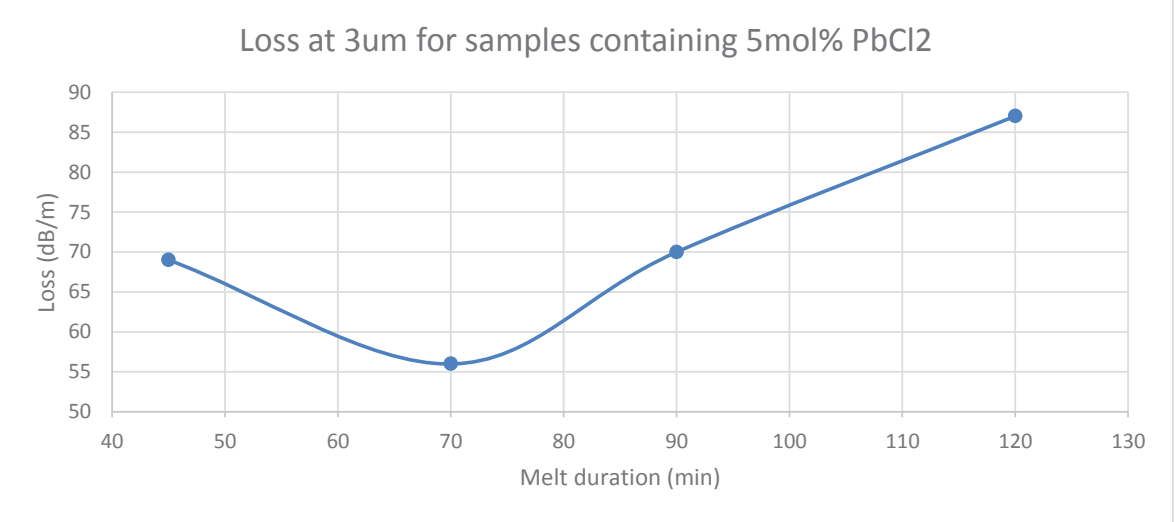


Fig. 9. Plot between the OH loss at 3um and melt durations for 4 samples containing 5 mol% PbCl2

3.3 Fiber loss (unstructured fibre

The transmission loss at 1.55um was measured in the drawn fiber using the standard cut-back technique. Around 5m of fiber was coupled into a light source and directed to a spectrum analyzer and cutbacks averaging to 1.5m per cutback were measured for the transmission efficiency. Loss of 0.99dB/m was observed at 1.55um wavelength.

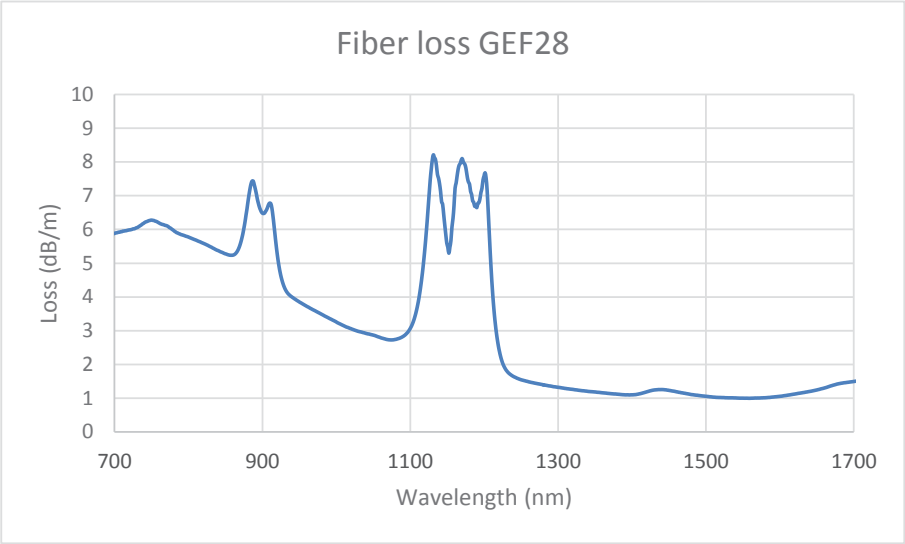


Fig. 10 Loss of unstructured GPGN fiber

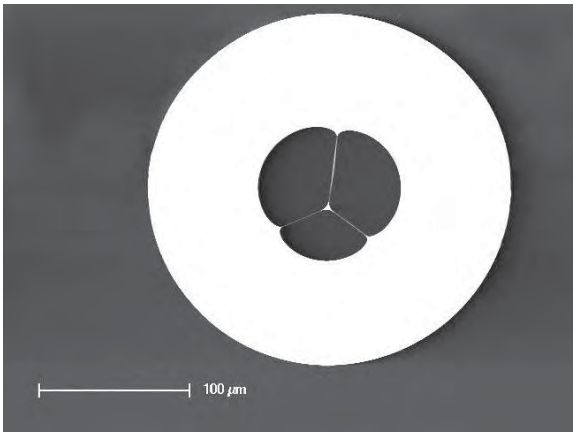
References:

1. *Nature Photonics* **4**, 576 - 577 (2010) doi:10.1038/nphoton.2010.173
2. H. Ebendorff-Heidepriem, C. Schiele, A. Winterstein, L. Wondraczek, D. G. Lancaster, D. J. Ottaway, and T. M. Monro, "New germanate glasses for infrared fibre applications," in Proceedings of the 37th Australian Conference on Opt. Fibre Technol., paper no. 518.00 (Sydney, Australia, Dec 2013)
3. X. Jiang, J. Lousteau, and A. Jha, "The Structural, Thermal, and Opt. Analyses of Multicomponent Germanium Oxide Glasses for Engineering Mid-Infrared Fiber Chemical Sensing," J. Am. Ceram. Society 93(10), 3259–3266 (2010)
4. Raw materials purification for the development of high performance infrared transmitting germanate glass fibres, *Glass Technology* 11/2009; 50(6):315-318)
5. Fluorogermanate glass with reduced content of OH-groups for infrared fiber optics, *Xin Jiang* , *Joris Lousteau*, *Shaoxiong Shen*, *Animesh Jha*, *Journal of Non-Crystalline Solids* *Volume 355, Issues 37–42*, 1 October 2009, Pages 2015–2019

Characterisation of GEF-35 Wagon Wheel fibre (GPGN)

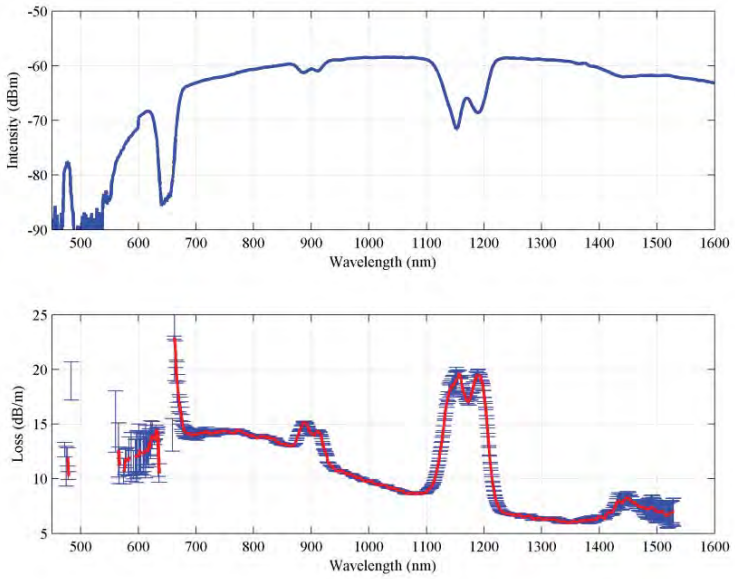
The fibre in this report is a WW fibre made of GPGN:Ho glass. This fibre was the culmination of 3 wagon wheel fiber draw (GEF 33, 34 and 35).

The SEM image of the cross-section of GEF 35 fibre is shown below. The core size of this fibre is around 3 microns in diameter.



Loss measurement (white light source)

The boardband loss of the fibre was measured using the cut-back method with a halogen light bulb as the light source.

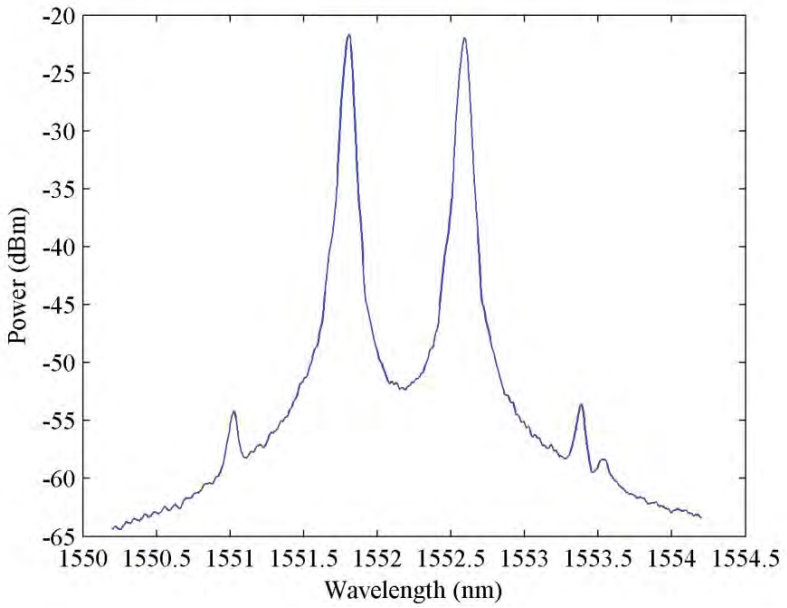


About 1 meters of fibre is used in this measurement, with the equipment available, only a small amount of light was coupled into the core of the fibre. To increase the measurement accuracy, the fibre was coated with carbon DAG to remove cladding light. During the measurement, the fibre was cut manually. Each cut back is about 10 cm. Only 5 cut back was possible before the cladding light intensity became significant. The alignment of the fibre was centred on 1 micron. Therefore, the measurement error is at minimum around 1 micron.

The loss profile matches with the profile of bare fibres and the loss value at 630 matches with the spot loss measurement done by Naveed.

Nonlinearity measurement

Nonlinearity of the fibre is measured using the Boskovic dual-CW method. Two CW co-polarised lasers with very wavelength separation were used. Sidebands were generated through nonlinear process. The ratios between the centre peaks and the sidebands were measured for different input power and the nonlinear phase change is calculated afterwards.



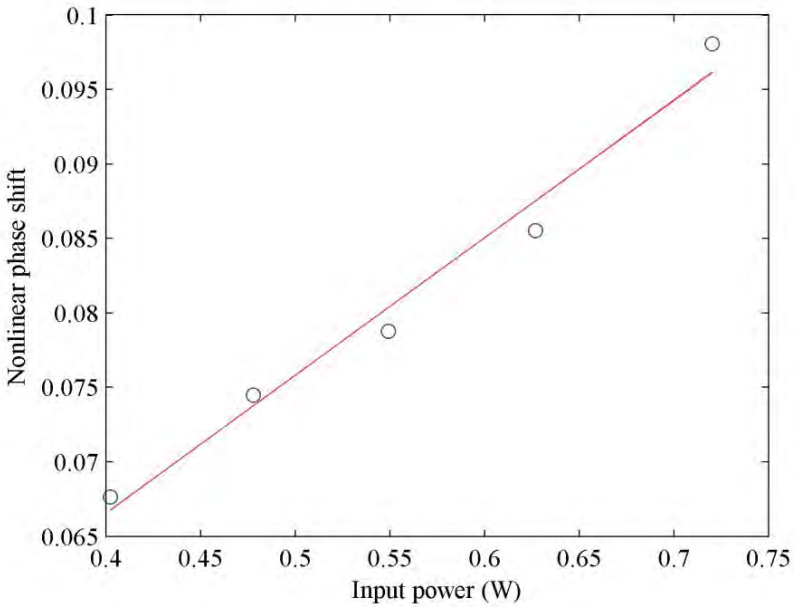
The nonlinear phase ϕ is defined as

$$\varphi = 2\gamma P_{avg} L_{eff}$$

Therefore, the nonlinearity of the fibre γ is

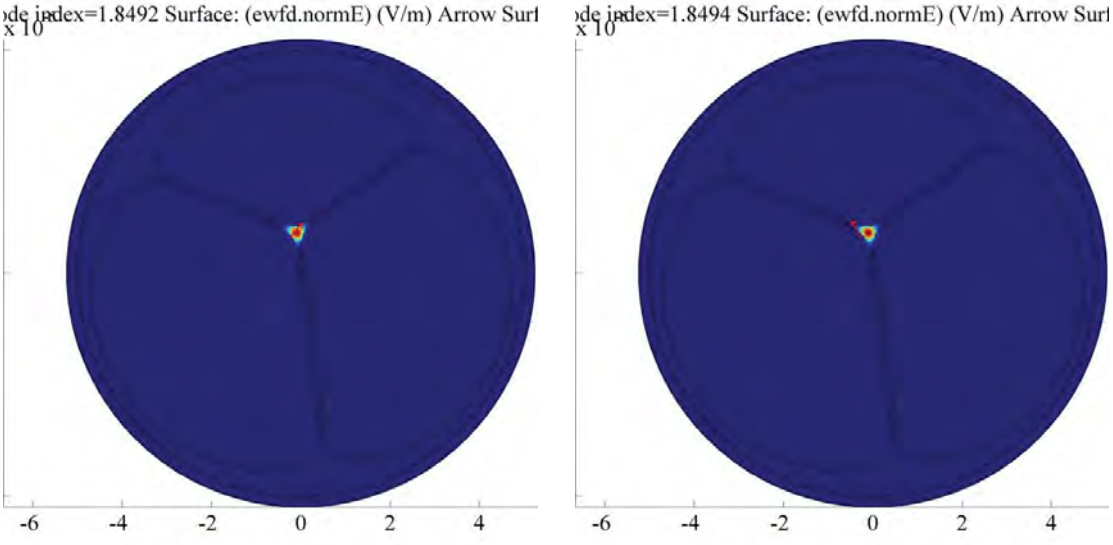
$$\gamma = \frac{\varphi}{2P_{avg}L_{eff}}$$

where P_{avg} is the average power measured in experiment.



A linear fit is performed on the nonlinear phase and input power. The slope of the fit is equal to ϕ/P_{avg}. The calculated nonlinearity of this fibre is 160 $W^{-1}km^{-1}$.

Simulations were also done based on the SEM image. The refractive index (1.87) at 1550 nm and n2 (57e-20) of the glass were obtained from http://dx.doi.org/10.1364/OME.3.001488



Effective refractive index Neff=1.849237854304498 and 1.849410496390415

Confinement loss CL=9.716008688750180e-12 and 2.470171179441403e-14 dB/km

Mode area A=7.518363073831391 and 7.545294576835833 um^2

Nonlinearity γ= 309.4861381689612 and 308.9632523263966 $W^{-1}km^{-1}$

The measured nonlinearity is smaller than the calculated value. It can be due to the error in the measurement. In order to have accurate measurement, we need a nonlinear phase much bigger than 0.1. However, given the loss of the fibre, we do not have enough pump power.

Conclusions

This project undertook an investigation of germanate glasses to identify a more stable composition to allow realisation of complex microstructured fiber geometries. Using a combination of glass analysis techniques, this 18 month project by a team of researchers found that germanate based on 56%GeO_2-31%PbO-4%Ga_2O_3-9%Na_2O (GPGN) had the lowest occurrence of surface oxidation, and bulk crystallisation under thermal cycling. Based on this criterion we optimised the fabrication conditions for GPGN (a relatively new glass), so that OH- impurities were reduced and we achieved a bulk glass loss of ~ 1 dB/ m. As this is a relatively new glass, we then conducted an investigation to determine the thermal and gas environment conditions to achieve microstructured preform fabrication using extrusion, and fibre drawing.

We were successful in fabricating holmium doped microstructured 'wagon wheel' fibres, designed for laser operation at ~2100 nm. However due to the use of poor quality chemicals with unknown contaminants (the best commercially available), we had the added challenges of high bulk glass loss and possibly unknown contaminants influencing glass stability.

Laser operation was attempted and due to high fiber loss (~ > 5 dB/m, unknown reasons at this time) threshold was not reached. We conducted non-linear measurements of this fiber and determined that it is commensurate with standard germanate fiber and has a non-linearity approximately ~ 100 x that of silica. The combination of reasonable transmission between 1300 and 2700 nm and high non-linearity indicates this fiber (subject to loss and contaminants being reduced) is potentially suitable for non-linear application such as supercontinuum and four-wave mixing where short fiber lengths can be used.

We are confident that germanate based fibers will make substantial impact on the field of heavily doped microstructured fiber lasers operating in the 1.5 to 2.7 µm spectral region, if low-loss fiber can be realised. The glaring reality is that without substantial investment in materials purification to reduce OH^- contamination, and ultimately commercial availability of pure starting chemicals, germanate fiber developed by small university research groups and small companies will struggle to meet application requirements due to high losses causing poor performance and unknown contaminants effecting glass stability.

Publications resulting from this work

Two papers are under preparation

1. 'Oxidation induced surface scattering in germanate glass under thermal cycling', Jiafang Bei, Ahmed Naved, David G Lancaster, Heike Ebendorff-Heidepreim. In preparation
2. 'Melt quench fabrication of low-loss germanate based glass for laser non-linear application', Ahmed Naved, Jiafang Bei, David G Lancaster, Heike Ebendorff-Heidepreim. In preparation